

A new critical point and time dependence of bond formation probability in sol–gel transition: a Monte Carlo study in two dimension

E. Tüzel, M.S. Özmetin, Y. Yılmaz, Ö. Pekcan*

Department of Physics, Istanbul Technical University, Maslak, Istanbul, 80626, Turkey

Received 4 January 1999; received in revised form 4 March 1999; accepted 13 May 1999

Abstract

In the sol–gel phase transitions of polymeric systems, gelation is generally being monitored against time t during in situ fluorescence experiments where the relation between bond formation probability p and t is unknown and has to be determined. In this study, the critical exponents β , γ and ρ of power law relations of the degree of polymerization (DP_w), the gel fraction (G) and the radius of gyration (R) were obtained, using Monte Carlo simulations in two dimension, respectively. A new critical point, p_m , was defined in order to calculate the critical exponents more accurately. The relation between p and t for four functional crosslinkers was examined and found to be linear at the critical region. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Two classes of polymers can be obtained if a small amount of crosslinker is used in the synthesis of polymerization. If the reaction time t is relatively short and below, but close to a characteristic time t_c then we obtain branched polymers in the solution, usually called a sol, that forms a viscous solution. These branched polymers are large but finite clusters of monomers. On the other hand, if the reaction time is larger than t_c , a very large solid network of connected monomers appears, that is usually called a gel. Gelation is the phase transition from the sol phase to the gel phase. Critical phenomena are those which occur exactly in the phase transition or asymptotically close to it.

Percolation offers a particularly simple and yet

detailed picture in terms of which one may seek to understand gelation [1,2]. In the language of percolation, one may think of monomers as occupying the sites of a periodic lattice, and the chemical bonds as corresponding to the edges joining these sites randomly with some probability p . The conversion factor p is the ratio of actual number of bonds that have been formed between the monomers, to the total possible number of such bonds. The gel point can be identified with the percolation threshold p_c , where, in the thermodynamic limit, the incipient infinite cluster starts to form; and the system behaves viscoelastically [3,4]. The percolation theory can predict critical exponents of β , γ and ρ for the gel fraction, G , weight average degree of polymerization, DP_w , and radius of gyration, R , respectively, near the gel point [1]. The scaling behavior of these and related quantities is defined as a function of $|p - p_c|$.

The conversion factor p is clearly a function of time. However, it can also depend on the temperature, the concentration of monomers or the concentration of

* Corresponding author. Tel.: +90-0212-285-3213; fax: +90-0212-285-6366.

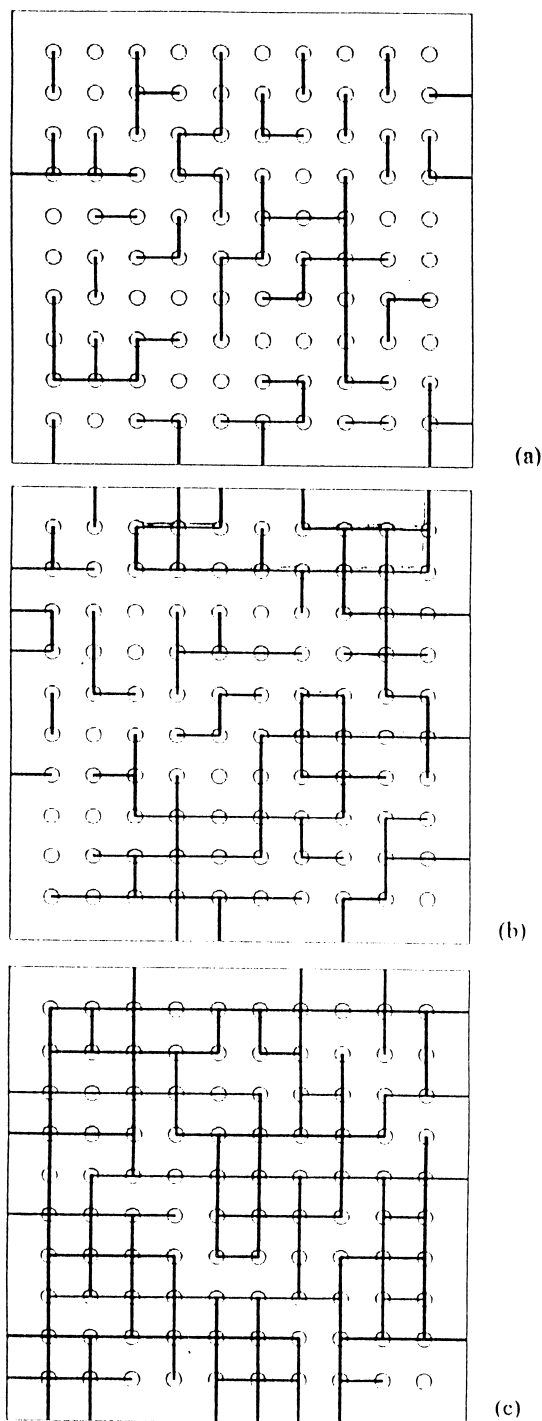


Fig. 1. Sample square lattices of size $L = 10 \times 10$ showing Monte Carlo simulations: (a) $p < p_c$, (b) $p = p_c$ and (c) $p > p_c$.

crosslinking agents necessary for bond formation, experimentally one usually starts with a fixed composition and monitors the process in time.

Recently in situ fluorescence technique was used to monitor the sol–gel phase transition in free radical crosslinking copolymerization [5–9] of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM). Gelation was monitored in real time t with the variation of fluorescence intensity I of the pyrene molecules against time. β and γ exponents were determined from $\log I$ versus $\log|t - t_c|$ plots of these data. However, the time dependence of bond formation probability, p , is always in question and has to be known.

In this work, our aim is to study the linearity between bond formation probability p and time t for the region near the gel point. Thus gelation is studied by employing percolation approach and the time dependence of bond formation probability p , is determined using Monte Carlo simulations on a square lattice of various lattice sizes. A new critical point, p_m , will be determined rather than p_c , which provides better accuracy in calculating the critical exponents β , γ and ρ especially while studying with smaller lattice sizes.

2. Theoretical considerations

The linkage process for polymerization can be described by percolation and Fig. 1 may be most instructive in bond percolation problems. For $p = 0$, no bonds have been formed and all monomers remain isolated from each other. However, at the other extreme, i.e., for $p = 1$, all the possible bonds have been formed and all the monomers of the system have clustered into one infinite network and no sol phase left. Usually, there is a sharp phase transition at some critical point $p = p_c$, where a percolating cluster appears. Thus, for $p < p_c$ only a sol exists, but for $p > p_c$ both sol and gel are present together [2].

During the initial period of reaction, crosslinkers and monomers start to react and form clusters of average size S , which can be defined by a size distribution function n_s ,

$$S = \frac{\sum_s s^2 n_s}{\sum_s s n_s} \quad (1)$$

where the average number n_s of s -clusters (normalized as number per f -functional monomer) defines the critical exponent τ at the gel point and the critical amplitude q_0 by [1]

$$n_s(p = p_c) = q_0 \cdot s^{-\tau} \quad s \rightarrow \infty \quad (2)$$

The weight average degree of polymerization DP_w (or weight average molecular weight M_w) is given by,

$$DP_w = B(p_c - p)^{-\gamma} \quad p \rightarrow p_c^- \quad (3)$$

where γ and B are the critical exponent and the amplitude of this power law relation, respectively. The quantity DP_w is the analog of S , the average size of the percolation clusters defined by Eq. (1).

The correlation or connectivity length ξ of branched polymers diverges as p_c is approached. Above p_c the correlation length of polymers can be interpreted as the mesh size of the gel network. Below p_c the correlation length is the typical radius of the clusters in the sol phase.

The spatial extent of a cluster is conveniently defined by the radius R_s of gyration,

$$R_s^2 = \frac{1}{s} \sum_{i=1}^s r_i^2, \quad s \rightarrow \infty, p \text{ fixed} \quad (4)$$

for p above, at and below p_c , this sum runs over all s monomers in the macromolecule where r_i is the distance of each monomer center from the center-of-mass of the macromolecule. R_s is also given by a power law relation

$$R_s = C \cdot s^\rho, \quad p = p_c, s \rightarrow \infty \quad (5)$$

where s is defined as the number of monomers in the infinite cluster at $p = p_c$. Here, ρ is the critical exponent which refers to the reciprocal of fractal dimension, D_f , and C is its critical amplitude.

The infinite cluster is believed to be a self-similar object since all structural elements, i.e., single connecting bonds, loops, dangling ends etc., are critical quantities. Their numbers diverge at p_c , so that they appear on all scales of observation [10].

The probability that an f -functional monomer belongs to the infinite network is equal to the gel fraction and is non-zero only for p above p_c

$$G = A(p - p_c)^\beta, \quad p \rightarrow (p_c^+) \quad (6)$$

Table 1
Values of the critical exponents and fractal dimension for two and three dimensional system [2]

	$d = 2$	$d = 3$
D_f	91/48	2.52
β	5/36	0.41
τ	187/91	2.18
γ	43/18	1.80

with a critical exponent β , and the asymptotic proportionality factor A which is referred to as the critical amplitude [1].

The values of the quantities D_f , β , τ , γ in two- and three-dimensions are summarized in Table 1.

3. Monte Carlo simulations

In Monte Carlo simulations on square lattices a method which is similar to Hoshen–Kopelman algorithm [11] is used. In the algorithm, all monomers in the percolation lattice are labeled in such a way that monomers with the same label belong to the same cluster and different labels are assigned to different clusters. When a bond is formed randomly between the two monomers, both monomers form a cluster with the same label. Addition of bonds to this cluster uses the same label. The larger cluster formed by the combination of two smaller clusters with different labels uses one of the labels of the forming smaller clusters. If the same label happened to be at opposite sides of the lattice, a percolating cluster is formed at which p_c is determined.

3.1. Critical point and critical exponents

In the simulations the critical point p_c is determined for a lattice of sizes $L \times L$ from 50×50 to 600×600 and it is observed that p_c approaches to a value smaller than that of the theoretical value [12,13], $p_c = 0.5$, as

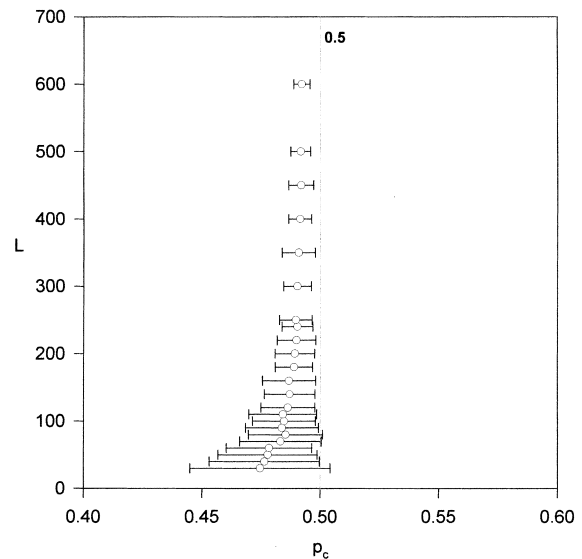


Fig. 2. Plot of the average critical point, p_c values versus lattice size, L for square lattices of various sizes, where p_c approaches to its theoretical value, 0.5.

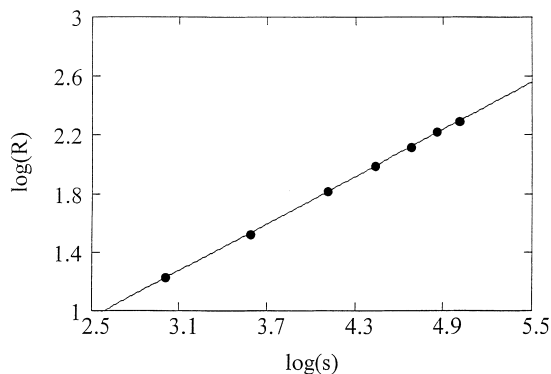


Fig. 3. The log–log plot of R_s versus s obtained for square lattices of various sizes. The slope of the line produces the value of ρ .

shown in Fig. 2. This difference is due to the selection of the boundary conditions in the lattice used. In our lattice all the sites, including the ones at the boundaries, are capable of making four bonds. Since the contribution of the bonds at the boundaries to the infinite cluster is smaller than their contribution to the maximum number of bonds, this boundary condition, which is more realistic for polymerization, causes a smaller p_c value.

Here, at least two hundred runs of simulations have been performed for each lattice size from which the average p_c value is determined. Error bars in Fig. 2 are calculated using the typical standard deviation formula:

$$\Delta p_c = \sqrt{\frac{\sum_{i=1}^N (p_c - \bar{p}_c)^2}{N}} \quad (7)$$

In order to test the correctness of the model Monte

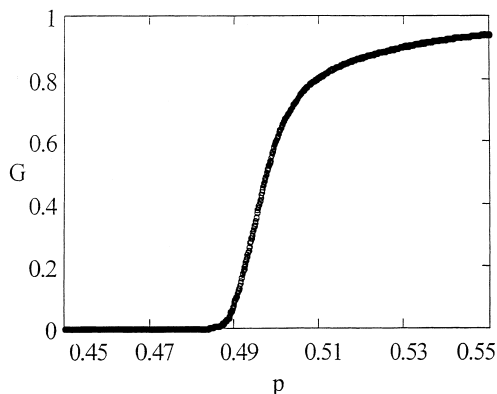


Fig. 4. The plot of average G versus p for square lattice of size 600×600 .

Carlo simulation, the radius of gyration, R_s of the infinite cluster was determined at the percolation threshold for all lattice sizes. A critical exponent, ρ was produced using the log–log plot of Eq. (5) which was plotted in Fig. 3. The slope of the linear curve in Fig. 3 provides $\rho = 0.53$ which is quite similar to the theoretical value of $48/91$. Since the reciprocal of ρ is known as the fractal dimension D_f , the relation $\rho = D_f^{-1}$ was used to produce D_f value and found to be 1.89 which is quite familiar by the reader of this subject.

The relation between G and p obtained from Monte Carlo simulations is shown in Fig. 4 for the lattice size of 600×600 which was obtained from the simulations of more than hundred runs. The exponent β can be produced using the logarithmic form of Eq. (6) as

$$\log(G) = \log(A) + \beta \cdot \log(p - p_m) \quad (8)$$

However, one must consider the importance of determining the exact place of the critical point besides the fact that all p_c values are the averages obtained using many simulations having quite low percentage of errors. Here it is important to note that during the determination of values β , a small shift in p_c results in a large shift in β , which must be taken into account. In other words there are many straight lines which all fit well to Eq. (8) to produce the exponent β . In order to overcome this difficulty a new critical point, p_m , is defined which produces β values very close to its theoretical value. The chosen p_m point then can be tested by measuring the other critical exponent, γ which is defined in Eq. (3). The relation between DP_w and p is shown in Fig. 5 and the logarithmic form of Eq. (3) is given below

$$\log(DP_w) = \log(B) - \gamma \cdot \log(p_m - p) \quad (9)$$

from which the critical exponent γ can be determined.

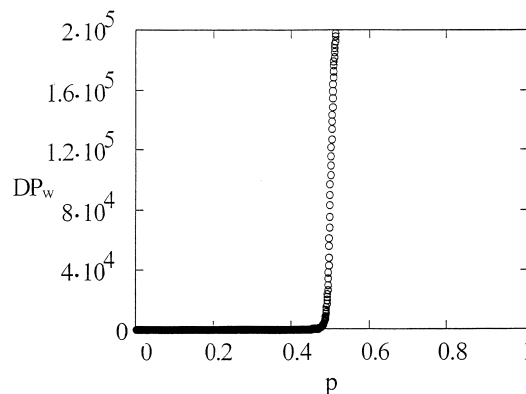


Fig. 5. Plot of the average DP_w versus p obtained from square lattice of size 600×600 .

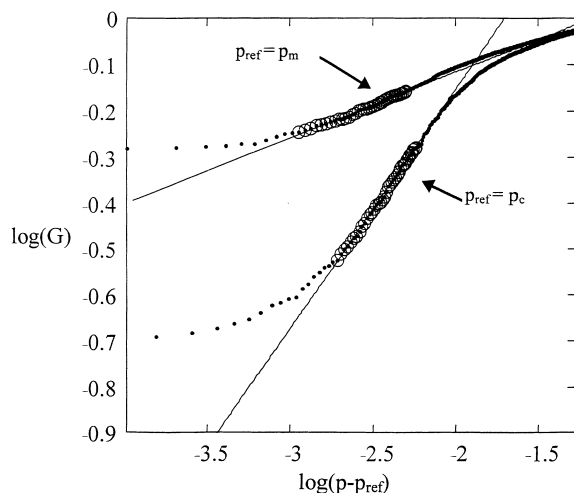


Fig. 6. The log–log plot of G versus p obtained from square lattices of size 600×600 . The two slopes correspond to the values of β obtained using p_c and p_m .

Now using Eqs. (8) and (9) one can determine the p_m which gives both critical exponents very close to their theoretical values. The log–log plot of Eqs. (8) and (9) are shown in Figs. 6 and 7, respectively. As seen from Fig. 6, there exists a difference between the slopes obtained using the two points p_c and p_m . Similarly the exponent γ was obtained from the slope of the line in Fig. 7. The values of β and γ calculated using the above graphs are listed in Table 2 which are comparable to the theoretical β and γ values. From these values we concluded that one should take p_m as the critical point instead of using the critical point p_c , to obtain meaningful β and γ values. The critical exponents calculated using p_m , approach their theoretical values as the lattice size increases (see Figs. 8 and 9).

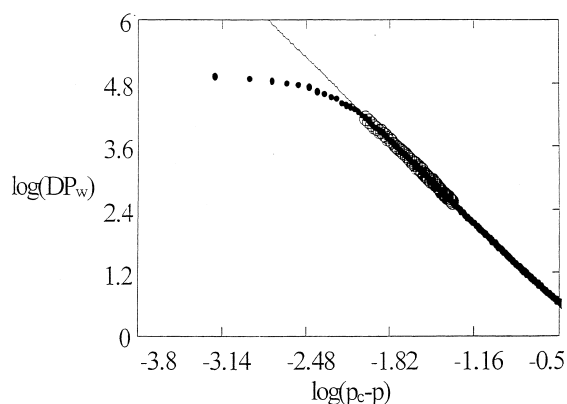


Fig. 7. The log–log plot of DP_w versus p obtained from square lattices of size 600×600 . The slope of the line corresponds to the value of γ obtained using p_m .

Table 2

The critical exponents β and γ calculated at the points p_c and p_m for lattice of size $L = 600 \times 600$

Critical point	β	γ
$p_c = 0.492184$	0.519544	2.110911
$p_m = 0.497700$	0.139704	2.371851

In order to determine the exact place of the critical point, a second method, which is easier than the previous one, can be used. The first derivative of the G versus p is plotted in Fig. 10 which provides further information about the critical point. As seen from Fig. 10, the point p_m is at the maximum of the dG/dp curve. Thus, the point p_c falls into the left-hand side of the maximum curve where the phase transition has not yet started.

3.2. Relation between p and t

As stated before, polymerization is monitored against time, t during in situ fluorescence experiments. In order to model the sol–gel phase transition using the power law relations expressed in Eqs. (3), (5) and (6), the relation between p and t must be known. This relation is determined by using a time-dependent algorithm in the Monte Carlo simulations. Instead of using the built-in clock of the computer, which is not accurate enough for these simulations, a time counter is used. After each successful bond formation this counter increments one step and therefore the time elapsed during the reaction increases by one step. Eventually the number of bonds also increases by one step. When both the number of bonds and the time increase by one step, nothing is unusual. If a bond is not formed successfully between two neighboring monomers, the time counter increments one step while the number of bonds remain the same. Above the percolation

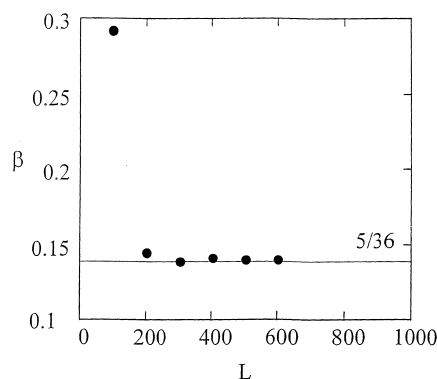
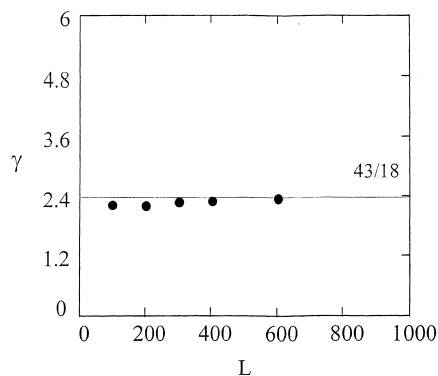


Fig. 8. Plot of β versus L .

Fig. 9. Plot of γ versus L .

threshold the counter time increases rapidly, however the number of bonds increase at a much slower rate.

The relation between p and t for a lattice of size 600×600 is given in Fig. 11. By knowing that the critical exponents are calculated below and above p_c in the critical region (see Fig. 11) which is defined as [14]

$$10^{-2} < \left| 1 - \frac{p}{p_c} \right| < 10^{-1} \quad (10)$$

Thus, it is sufficient to calculate the function, $p(t)$ in this critical region. Here, polynomial fitting can be used to determine the linearity between p and t . The $p(t)$ function normalized in the critical region is given by

$$p(t) = a \cdot t^2 + b \cdot t \quad (11)$$

where $0 \leq t \leq 1$ and $0 \leq p \leq 0.55$. Polynomial fitting produces the $a = -0.054 \pm 0.032$ and $b = 0.604 \pm 0.032$ values which present the linearity of $p(t)$ at the critical region.

Although the above relation is obtained from a lattice of size 600×600 , the slight differences in the $p(t)$

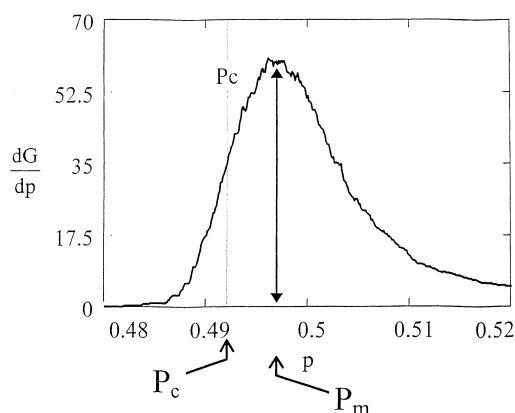
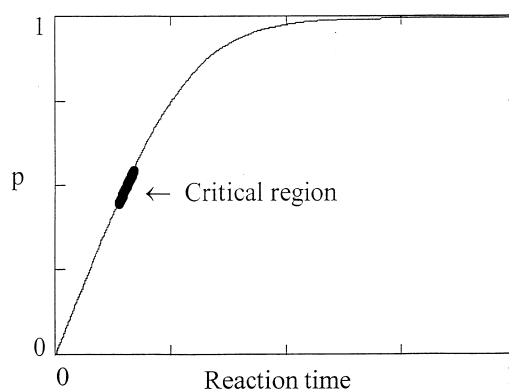
Fig. 10. Plot of dG/dp versus p for lattice of size 600×600 .

Fig. 11. The relation between p and t for a lattice of size 600×600 . Both p and the reaction time, t are normalized. Dark line indicates the critical region around p_c as $10^{-2} < \left| 1 - \frac{p}{p_c} \right| < 10^{-1}$.

functions for different lattice sizes are found within the error limits. The function does not differ when the size increases. Error percentage is very small because of the accuracy of the time-dependence algorithm. Thus, the function $p(t)$ can be expected as linear in the critical region.

It is very difficult to make a connection between the counter time and real time. However, one can perform Monte Carlo simulations using this time algorithm and calculate the critical exponents using t instead of p . Gel fraction, G versus reaction time produced with Monte Carlo simulations is shown in Fig. 12. Here one has to notice the similarities between Figs. 4 and 12. From here we conclude that the linear relation between p and t which was assumed and used in our early real time fluorescence experiments [5–9], can be acceptable in the critical region, where β and γ exponents are obtained.

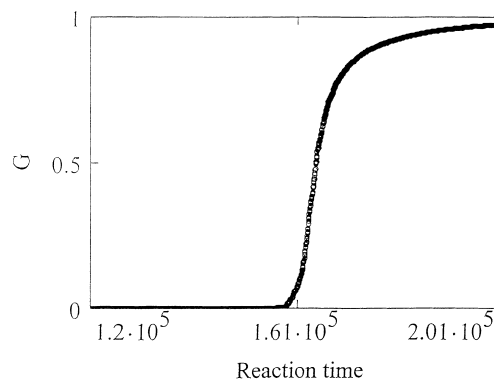


Fig. 12. The plot of G versus time for a lattice of size 600×600 .

References

- [1] Stauffer D, Aharony A. An introduction to percolation theory, revised 2nd ed. London: Taylor and Francis, 1994.
- [2] Sahimi M. Applications of percolation theory. London: Taylor and Francis, 1994.
- [3] Arbabi S, Sahimi M. *Phys Rev Lett* 1990;65:725.
- [4] Arbabi S, Sahimi M. *Phys Rev B* 1993;47:695.
- [5] Pekcan Ö, Yılmaz Y, Okay O. *Chem Phys Lett* 1994;229:537.
- [6] Pekcan Ö, Yılmaz Y, Okay O. *Polymer* 1996;37:2049.
- [7] Pekcan Ö, Yılmaz Y, Okay O. *J Appl Polym Sci* 1996;61:2279.
- [8] Pekcan Ö, Yılmaz Y. Fluorescence method for monitoring gelation and gel swelling in real time. In: Reltig W, Strehmel B, Schrader S, Seifert H, editors. *Applied fluorescence in chemistry, biology and medicine*. Berlin-Heidelberg: Springer-Verlag, 1999. p. 371–87 (Chapter 15).
- [9] Yılmaz Y, Erzan A, Pekcan Ö. *Phy Rev E* 1998;58:7487.
- [10] Stanley HE, Ostrowsky N. *On growth and form*. Amsterdam: Elsevier, 1985.
- [11] Hoshen L, et al. *J Phys* 1979;A12:1285.
- [12] Sykes MF, Essam JW. *J Math Phys* 1964;5:1117.
- [13] Kesten H. *Comm Math Phys* 1980;74:41.
- [14] Stauffer D, Coniglio A, Adam M. Gelation and critical phenomena. In: *Advances in polymer science*, vol. 74. Berlin-Heidelberg: Springer-Verlag, 1982. p. 44.